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(54) PROCESS FOR PRODUCING HIGHLY CHLORINATED HYDROCARBONS

(71) We, SUMITO CHEMICAL COMPANY, LIMITED, a Japanese Company, of No. 15, Kitahama 5-Chome, Higashi-Ku, Osaka-Shi, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing highly chlorinated hydrocarbons by oxychlorination.

It is known that a molten salt catalyst comprising a copper chloride or a mixture of a copper chloride and potassium chloride can be used in the production of chlorinated hydrocarbons, for example, monochloroethylene, 1,2-dichloroethane and monochloroethane from saturated aliphatic hydrocarbon by an oxychlorination reaction as disclosed in U.S. Patent Specification No. 3,557,229. However, the molten salt catalyst disclosed in the above U.S. Patent Specification cannot be used for producing a product containing predominantly highly chlorinated hydrocarbons such as tetrachloromethane, trichloroethylene and tetrachloroethylene because of its low activity. Also, the above known process has a disadvantage in that the conversion of a feed hydrocarbon into the desired chlorinated hydrocarbon is low.

Our British Patent Specification No. 1,373,296 as proposed to be amended describes and claims a process for producing highly chlorinated hydrocarbons by oxychlorination from a saturated or unsaturated aliphatic hydrocarbon and/or partially chlorinated hydrocarbon thereof using as a catalyst an unsupported molten material consisting of (1) 95 to 50 mole % of a copper chloride or of a mixture of a copper chloride and an alkali metal and/or an alkaline earth metal chloride and (2) 5 to 50 mole %, of at least one chloride of a metal selected from iron, manganese, palladium and the

rare earth metals, the reaction conditions being chosen to achieve a conversion of at least 98 mole % of the starting hydrocarbons to a product containing a major proportion of highly chlorinated hydrocarbons. In this previous process, the proportion of the metal chloride (2) above is limited to not less than 5 mole % in order to prevent decomposition of the unsaturated aliphatic hydrocarbon used as a feed material. However, as a result of further investigations on the catalyst in greater detail, it was unexpectedly found that, when saturated aliphatic hydrocarbons, partially chlorinated saturated or unsaturated aliphatic hydrocarbons are used as a feed material, unsupported molten salt catalysts containing less than 5 mole % of the metal chloride (2) above can also be used effectively with high selectivity and high oxychlorination activity.

According to the present invention there is therefore provided a process for producing highly chlorinated hydrocarbons (as herein defined) which comprises contacting a hydrocarbon feed material containing at least one compound selected from saturated aliphatic hydrocarbons and partially chlorinated saturated or unsaturated aliphatic hydrocarbons with oxygen and, as a chlorine source, hydrogen chloride or chlorine or a mixture of hydrogen chloride and chlorine, in the presence of an unsupported molten salt catalyst maintained at a temperature of from 250 to 650°C to oxychlorinate said feed material, said molten salt catalyst comprising the following components: (A) more than 95, but not more than 99.5, mole % of a copper chloride or a mixture of a copper chloride and at least one chloride selected from alkali metal chlorides and alkaline earth metal chlorides and (B) less than 5, but not less than 0.5, mole % of at least one chloride of a metal selected from palladium and rare earth metals, the reaction conditions being chosen to achieve a conversion of at least 92 mole % of the starting hydrocarbons to a product

containing a major proportion of highly chlorinated hydrocarbons.

The process of this invention is effective for the production of highly chlorinated hydrocarbons which are defined as those having at least one carbon atom per molecule to which at least two chlorine atoms are bonded, such as trichloromethane, tetrachloromethane, trichloroethylene, tetrachloroethylene and trichloroethane. The unsupported molten salt catalyst used in the present invention has a high selectivity and a high activity and is obtained by incorporating a small proportion of the chloride (B) into the chloride (A).

The alkali metal chlorides which can be used in the present invention include lithium chloride, sodium chloride and potassium chloride, and the alkaline earth metal chloride is preferably magnesium chloride.

These alkali metal or alkaline earth metal chlorides are mainly used to lower the melting point of the unsupported molten salt catalyst. Usually, the alkali metal chloride and/or the alkaline earth metal chloride is used as a mixture with a copper chloride in an amount less than 2 moles, preferably less than 1 mole, per mole of the copper chloride.

Examples of the metal chloride (B) include palladium chloride, lanthanum chloride, cerium chloride, praseodymium chloride and neodymium chloride. These chlorides can be used either alone or as a mixture.

The compositions of the unsupported molten salt catalyst used in the present invention are selected in such a manner that the resultant catalyst has a melting point lower than about 650°C.

Suitable examples of the hydrocarbon feed material which can be used in the process of this invention are saturated aliphatic hydrocarbons having from 1 to 4 carbon atoms such as methane, ethane, propane and butane, partially chlorinated saturated or unsaturated aliphatic hydrocarbons having from 1 to 4 carbon atoms such as monochloromethane, dichloromethane, monochloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,4-dichlorobutane, monochloroethylene and dichloroethylene.

Suitable chlorine sources which may be used in the present invention are hydrogen chloride including an aqueous hydrochloric acid, chlorine gas or a mixture thereof.

In carrying out the process of this invention, the proportion of hydrocarbon feed material, chlorine source and oxygen is not critical and can easily be determined experimentally depending upon the hydrocarbon starting material to be fed and the chlorinated hydrocarbon desired as a product. Generally, the chlorine source can be used in a proportion of from 0.1 to 20 moles calculated as chlorine gas (Cl_2) per 1 mole of the hydrocarbon feed material, and the proportion of chlorine (Cl_2) and oxygen can be from 0.05

to 1 mole of oxygen per 1 mole of chlorine. When hydrogen chloride is used as a chlorine source, the proportion can be from 0.05 to 1 mole of oxygen per 1 mole of hydrogen chloride.

The term "oxygen" used throughout the specification of this invention refers to molecular oxygen gas alone or a mixture of molecular oxygen and an inert gas. It is preferred to use oxygen alone or air.

In the process of this invention, the above-described molten salt catalyst is used in the unsupported molten state at a temperature of from 250 to 650°C, preferably of from 300 to 600°C. At a catalyst temperature below about 250°C, the conversion of the hydrocarbon feed material to the desired highly chlorinated hydrocarbon is remarkably lowered, and on the other hand, at a catalyst temperature higher than about 650°C, the hydrocarbon feed material tends to be decomposed or to become tarry thereby resulting in a loss of the hydrocarbon feed material.

As described previously, the process of this invention is carried out at a temperature at which the catalyst is in the molten state. Some of the catalyst systems used in the present invention are not in the molten state over the whole temperature range of from 250 to 650°C, i.e., some catalysts have a melting point of, for example, 400°C. In such case, the oxychlorination of this invention is carried out at a temperature between 400 to 650°C at which the catalyst is in the molten state.

In carrying out the process of this invention, the reaction pressure is not particularly critical, but, in general, the reaction is preferably carried out under a pressure of from 0 to 30 kg/cm² (gauge).

The oxychlorination of the feed material is preferably carried out by blowing the hydrocarbon feed material into the unsupported molten salt catalyst having the composition previously described or by passing the hydrocarbon feed material over the surface of the unsupported molten salt catalyst flowing down the surface of appropriate fillers. That is, the oxychlorination reaction can be effected in any manner as long as the hydrocarbon feed material to be oxychlorinated is effectively contacted with the unsupported molten salt catalyst. However, when the hydrocarbon feed material is introduced into the unsupported molten salt catalyst in the form of an admixture with molecular oxygen or a molecular oxygen-containing gas, some combustion reaction tends to occur thereby resulting in loss of the hydrocarbon feed material. It is therefore preferred that the hydrocarbon feed material, chlorine source and oxygen are introduced separately into the molten salt, but the use of a mixture of a hydrocarbon feed material and the chlorine source or a mixture of the chlorine source and oxygen

does not adversely effect the oxychlorination reaction of this invention.

The reaction of this invention may be carried out in various ways. In preferred embodiments, the reaction can be effected by introducing the hydrocarbon feed material, chlorine source and oxygen into one reactor containing an unsupported molten salt catalyst, or by introducing the hydrocarbon feed material alone or a mixture of the hydrocarbon feed material and the chlorine source into a chlorination reactor and separately introducing oxygen alone or a mixture of oxygen and a chlorine source into an oxidation reactor for the unsupported molten salt catalyst while recycling the unsupported molten salt catalyst between the two reactors. However, it is to be stressed that the process of this invention is not limited to the above specifically described ways.

As described above, the process of this invention makes it possible to produce highly chlorinated hydrocarbons such as trichloromethane, tetrachloromethane, trichloroethylene, tetrachloroethylene and trichloroethane in a high yield, compared with that obtainable in the production of chlorinated hydrocarbons from a hydrocarbon feed material by oxychlorination using a well-known molten salt catalyst, and is therefore extremely useful in industry. Also, the unsupported molten salt catalyst used in the present invention is characterized by its high ability to convert a hydrocarbon feed material into the desired highly chlorinated hydrocarbons as compared with that of the conventional molten salt catalyst. The unsupported molten salt catalyst of this invention has excellent advantages in that the formation of by-products due to the oxidation of the hydrocarbon feed material is remarkably decreased as compared with the production of chlorinated hydrocarbons by oxychlorination using the conventional catalyst supported on a carrier, and that the conversion of the hydrocarbon feed material into a highly chlorinated hydrocarbon can be remarkably increased. In addition, the unsupported molten salt catalyst makes it easy to control the oxychlorination reaction.

The present invention will now be further illustrated by the following Examples, in which all percentages, parts and proportions are by weight unless otherwise indicated.

EXAMPLE 1

Into a Pyrex* glass (a heat-resisting glass) reaction tube having an inside diameter of 60 mm a height of 500 mm and equipped with two gas-blowing glass tubes, the outlets of which were set 20 cm under the liquid level, were charged 695 cc of a molten salt comprising 3 mole % of neodymium chloride

and 97 mole % of a mixture of cuprous chloride, cupric chloride and potassium chloride (the molar ratio of the copper chlorides to potassium chloride was 7:3), and the molten salt was maintained at a temperature of 480°C. Methane was then introduced into the molten salt catalyst through one of the gas-blowing tubes at a rate of 80 cc/minute and, at the same time, a mixed gas of hydrogen chloride and air was introduced into the molten salt through the other gas-blowing tube at a rate of 320 cc/min of hydrogen chloride and 800 cc/min of air to effect oxychlorination continuously for 2 hours. The resultant gas discharged from the outlet of the reaction tube was collected using a condenser and a gas collecting apparatus and the reaction product was analyzed by gas chromatography.

The results obtained by the analysis showed as 95% conversion of methane, and a composition of the chlorinated product is shown in Table 1 below.

TABLE 1

Products	% by weight	
Monochloromethane	2.1	90
Dichloromethane	4.0	
Trichloromethane	8.4	
Tetrachloromethane	84.7	
Trichloroethylene	0.6	
Tetrachloroethylene	Trace	
Total	99.8	95

COMPARATIVE EXAMPLE 1

The oxychlorination reaction was carried out in the same manner as described in Example 1 but using ethylene as a starting material in place of methane.

The results indicated that the product comprised carbon, a high-boiling point tar-like material, CO and CO₂, and substantially no chlorinated hydrocarbon product was observed.

EXAMPLE 2

Into a Pyrex glass reaction tube having an inside diameter of 60 mm and a height of 600 mm and equipped with two gas-blowing tubes, the outlets of which were set 30 cm under the liquid level, were charged 862 cc of a molten salt comprising 1 mole % of neodymium chloride, 1 mole % of cerium chloride and 98 mole % of a mixture of cuprous chloride, cupric chloride and potassium chloride (the molar ratio of the copper chlorides and potassium chloride was 6:4), and the molten salt was maintained at 510°C. Ethane was then introduced into the molten salt catalyst through one of the gas-blowing tubes at a rate of 60 cc/min of ethane and, at the same time a mixed gas of hydrogen chloride and oxygen was introduced through

* Pyrex is a Registered Trade Mark.

the other gas-blowing tube into the molten salt catalyst, at a rate of 400 cc/min of hydrogen chloride and 200 cc/min of oxygen to effect oxychlorination continuously for 1.5 hours. The resulting gas discharging from the outlet of the reaction tube was cooled to -30°C and the reaction product was collected and analyzed.

The results obtained by the analysis showed a 97% conversion of ethane, and the composition of the chlorinated product is shown in Table 2 below.

TABLE 2

Products	% by weight
Monochloroethane	3.5
Monochloroethylene	2.1
1,2-Dichloroethane	1.5
1,1-Dichloroethane	1.3
Dichloroethylene	3.5
1,1,1-Trichloroethane	3.0
1,1,2-Trichloroethane	2.5
Trichloroethylene	8.3
Tetrachloroethylene	42.1
Tetrachloromethane	23.0
Others	9.2
Total	100.0

EXAMPLE 3

An oxychlorination reaction was carried out in the same manner as described in Example 1 but using propane as a hydrocarbon feed material which was fed at a rate of 40 cc/minute and a molten salt catalyst comprising 0.5 mole % of lanthanum chloride, 0.5 mole % of palladium chloride and 99 mole % of a mixture of cuprous chloride and cupric chloride maintained at a temperature of 500°C. After completion of the oxychlorination, the reaction product was collected and presented for analysis. The results showed a 95% conversion of propane and the composition of the chlorinated product is shown in Table 3 below.

TABLE 3

Products	% by weight
Monochloropropane	Trace
Monochloroethylene	0.2
1,2-cis-Dichloroethylene	0.2
1,2-trans-Dichloroethylene	0.2
1,1-Dichloroethylene	0.3
Tetrachloromethane	30.5
Trichloroethylene	6.6
Tetrachloroethylene	61.8
Total	99.8

EXAMPLE 4

Into a Pyrex glass reaction tube having an inside diameter of 60 mm and a height

of 900 mm equipped with two gas-blowing tubes were charged 1,516 cc of a molten salt comprising 2 mole % of neodymium chloride and 98 mole % of a mixture of cuprous chloride, cupric chloride and potassium chloride (the molar ratio of the copper chlorides and potassium chloride was 6:4), and the molten salt was maintained at a temperature of 470°C. Gaseous vinylidene chloride was then introduced through one of the gas-blowing tubes into the reaction tube at a rate of 0.004 mole/minute and, at the same time, hydrogen chloride and oxygen were introduced through the other gas-blowing tube into the reaction tube at a rate of 200 cc/minute and 50 cc/minute, respectively, to continuously effect the oxychlorination reaction for 1 hour. The gas discharging from the reaction tube was cooled to -30°C, and the collected reaction product was analyzed by gas chromatography. The results obtained by the analysis of the reaction product showed a 92% conversion of vinylidene chloride, and the chlorinated product was found to have a composition shown in Table 4 below.

TABLE 4

Product	% by weight
Tetrachloromethane	29.8
Trichloroethylene	11.1
Tetrachloroethylene	45.2
Others	13.9
Total	100.0

WHAT WE CLAIM IS:—

1. A process for producing highly chlorinated hydrocarbons (as herein defined) which comprises contacting a hydrocarbon feed material containing at least one compound selected from saturated aliphatic hydrocarbons and partially chlorinated saturated or unsaturated aliphatic hydrocarbons with oxygen and, as a chlorine source, hydrogen chloride or chlorine or a mixture of hydrogen chloride and chlorine, in the presence of an unsupported molten salt catalyst maintained at a temperature of from 250 to 650°C to oxychlorinate said feed material, said molten salt catalyst comprising the following components: (A) more than 95, but not more than 99.5, mole % of a copper chloride or a mixture of a copper chloride and at least one chloride selected from alkali metal chlorides and alkaline earth metal chlorides and (B) less than 5, but not less than 0.5, mole % of at least one chloride of a metal selected from palladium and rare earth metals, the reaction conditions being chosen to achieve a conversion of at least 92 mole % of the starting hydrocarbons to a product containing

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a major proportion of highly chlorinated hydrocarbons.

2. A process according to Claim 1, wherein said alkali metal chloride is lithium chloride, sodium chloride or potassium chloride.

3. A process according to Claim 1 or 2, wherein said alkaline earth metal chloride is magnesium chloride.

4. A process according to any preceding Claim, wherein component (A) is said mixture which comprises less than 2 moles of at least one chloride selected from alkali metal chlorides and alkaline earth metal chlorides per mole of copper chloride.

5. A process according to any preceding Claim, wherein said rare earth metals are lanthanum, cerium, praseodymium and neodymium.

6. A process according to any preceding Claim, wherein oxygen is contacted in a proportion of from 0.05 to 1 mole per mole of chlorine source.

7. A process according to any preceding Claim, wherein the chlorine source is contacted in a proportion of from 0.1 to 20 moles, calculated as Cl_2 , per mole of hydrocarbon feed material.

8. A process according to any preceding Claim, wherein said hydrocarbon feed material is methane, ethane, propane, butane, monochloromethane, dichloromethane, monochloroethane, 1,2 - dichloroethane, 1,1,2-trichloroethane, 1,4 - dichlorobutane, monochloroethylene or dichloroethylene.

9. A process for preparing highly chlorinated hydrocarbons as claimed in Claim 1 and substantially as herein described.

10. A process for preparing highly chlorinated hydrocarbons, substantially as herein described with reference to any one of the foregoing Examples of the invention.

11. Highly chlorinated hydrocarbons when prepared by a process as claimed in any preceding claim.

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